ELEMENTAL COMPOSITION STUDY OF PRE-COLONIAL CERAMICS FROM PANTANAL OF MATO-GROSSO DO SUL BY NEUTRON ACTIVATION ANALYSIS

M. P. Felicissimo
J. L. Peixoto
C. S. Munita

Resumo

Um estudo preliminar sobre a fonte de matéria-prima usada na fabricação dos artefatos cerâmicos dos sítios MS-CP-61 e MS-CP-71, localizados na borda oeste do Pantanal Sul Mato-grossense, foi realizado com base na determinação de elementos traço por análise por ativação com nêutrons. Através destas medidas foram determinadas as concentrações dos elementos: Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Ta, Tb, Th, U, Yb e Zn em 60 amostras, sendo 37 oriundas do sítio MS-CP-71, 15 do sítio MS-CP-61 e 8 amostras de argilas coletadas na região. Visando a obtenção de informações mais conclusivas, efetuou-se o tratamento estatístico dos dados obtidos por análise discriminante, que possibilitou verificar uma origem distinta para matéria-prima utilizada na confecção das cerâmicas provenientes dos dois sítios arqueológicos em estudo.

Palavras chaves:

neutron activation analysis; archaeometry; Pantanal; pottery; clay; discriminant analysis.

Abstract

A preliminary study of ancient ceramics raw material provenance from two archaeological sites located in the flood plains of Paraguai River, in Pantanal of Mato-Grosso do Sul, has been performed. Archaeological studies in this region began in 1990, with the classification of *c.a.* 200 sites. These archaeological sites have a large amount of ceramic material not only on the surface but also along a depth profile, where the most antique dating is 2.640 B.P. Both sites were characterized as long term settlements of great importance to the study of the ancient population that inhabited this area. The trace element concentration of the potsherds was measured by neutron activation analysis. In order to obtain more conclusive information, discriminant analysis was applied in the data treatment. The measured elements were Na, Lu, U, Yb, La, Th, Cr, Cs, Sc, Rb, Fe, Eu, Ce, Hf, and Tb. The composition analysis results enable to attribute a significant distinction to potsherds coming from the archaeological sites MS-CP-71 and MS-CP-61.

Keywords:

neutron activation analysis; archaeometry; Pantanal; pottery; clay; discriminant analysis.

Introduction

The present work is part of a study that aims shedding light on the technology applied by pre-colonial Indians who lived near the west border of Mato Grosso do Sul Pantanal, concerning the fabrication of their ceramic artifacts. Based on archaeometric studies it is of our interest to obtain information on the procedures applied by the ancient artisan in the pottery fabrication and to enable the recognition of an identity for this group of ceramics. In the part herein presented we have as a main objective the characterization of the pottery coming from two different archaeological sites regarding its elemental composition. Archaeological studies in this region began in 1990, with the classification of *c.a.* 200 sites. These archaeological sites present a large amount of ceramic material not only on the surface but also along a depth profile, where the most antique dating is 2.640 B. P.

The study of archaeological remains from sites of Pantanal, a nature preservation area located in the heart of South America, can contribute in a large extent to a better understanding of pre-colonial Indian populations that inhabited this region, since they seem not to be related to the Indian communities that lived in the area along the *luso-hispanic* colonization period **(PEIXOTO, 2003).** The pottery fabricated by these populations often has yellow, red and sometimes black surfaces very often with a dark grey bulk, which has been demonstrated to be a result of the drying and firing procedure of the pieces occasioned by "black heart" formation (**FELICISSIMO et al., 2004a**). The pottery under study presents different types of additives such as shells, sponge spicules and burnt bone (**FELICISSIMO et al., 2001**). A detailed investigation of the technology attained by pre-colonial populations, about which there is a lack on historical report, can be achieved through the characterization of their ceramic remains. Therefore an extensive work involving the study of this kind of archaeological material by means of physical and chemical analyses has been performed. The obtained results enable to answer questions regarding the age, fabrication process and the identity of the components present in the ceramic mass. In order to attain information about the methodology and the condition used in the fabrication process of these objects, morphological and mechanical analyses were applied. As a result of these studies it was possible to determine the existence of certain procedures applied by the artisans in the fabrication of the ceramic piece, as for example, the use of several kinds of additives. The assembling technique of the vessels and their firing procedure could also be clarified **(FELICISSIMO et al., 2004b)**. The ceramics compositional analysis by neutron activation analysis will be presented in the present work. The results indicate that potsherds from the archaeological sites MS-CP-71 and MS-CP-61 form two distinct groups regarding their elemental composition.

Different analytical techniques may be applied to determine trace elements concentration, such as ICP (**PILLAY and PUNYADEERA, 2001**), **EDXRF (HALL et al., 2002; DAVIS et al., 1998; SCOTT, 2001**), and INAA (**GLASCOCK, 1992; MUNITA et al., 2003; MUNITA et al., 2001**), among others. Within these techniques, INAA associated with the spectrometric gamma rays of high resolution have been preferentially used for the determination of the chemical composition of ceramic samples, since it presents several advantages such as better sensitivity, precision and accuracy (**BISHOP et al., 1990**). In this kind of study, analytical parameters have great importance, since there are small differences in the concentration of elements in the samples.

Thirty seven pottery samples from the archaeological site MS-CP-71 and fifteen from archaeological site MS-CP-61 were analyzed. The analysis by means of INAA enabled the concentration determination of fifteen elements. The data treatment was performed by means of discriminant analysis and in order to check a possible assemblage, the data for one clay source was added to the total data set. Based on the obtained results it was possible to verify the existence of two distinct pottery groups.

Experimental

Sample preparation and standards

The powder samples of the ceramic fragments were obtained by cleaning the outermost surface of the sherds and drilling to a depth of 2-3 mm, using a tungsten carbide rotary file attached to the end of a flexible shaft, with variable speed drill. Depending on the thickness, 3 or 5 holes were drilled as deep into the core of the sherd as possible without drilling through the walls (**MUNITA et al., 2001**). Prior to the analysis the material was dried in an oven at 105°C for 24h and stored in desiccators.

The Standard Reference Material NIST-SRM 1663b (Constituent Elements in Coal Fly Ash) was used as standard, and Brick Clay (NIST-SRM 679) and IAEA –Soil 7 (Trace Elements in Soil) were used as check samples in all analysis. These materials were dried in an oven at 105°C for 2h and stored in a desiccator before weighing (**MUNITA et al., 2003**).

Description of the method

In a few words, NAA method is based on the properties of nuclei, in which an incident neutron interacts with a nucleus of the target element. During the sample bombardment with neutrons a small fraction of the nucleus from each of the sample constituent elements will be transformed into an unstable radioactive isotope, which decays with a characteristic half-life. During the decay, these isotopes emit gamma rays with energies that are characteristic of each element. The measure of these gamma rays permits the qualitative and quantitative determination of the concentration of the elements present in the sample.

About 100 mg of ceramic or clay samples, NIST-SRM 1663b, Brick Clay and IAEA –Soil 7 were weighed in polyethylene bags and packed with aluminum foil. The samples and the reference material were irradiated in the pool research reactor, IEA-R1m, from the IPEN-CNEN/SP at a thermal neutron flux of about 5 x 10^{12} $n \cdot cm^{-2} \cdot s^{-1}$ for 8h.

Two measurement series were carried out using Ge (hyperpure) detector, model GX 2020 from Canberra, resolution of 1.90 keV at the 1332.49 keV gamma peak of ^{60}Co, with S-100 MCA of Canberra with 8192 channels. The elements Na, Lu, U, Yb and, La were measured after 7 days cooling time and Th, Cr, Cs, Sc, Rb, Fe, Eu, Ce, Hf and Tb after 25-30 days. The gamma ray spectra analysis and the concentrations were determined using the Genie-2000 Neutron Activation Analysis Processing Procedure from Canberra.

Results and Discussion

NAA is a highly sensitive technique, therefore the concentration of trace elements, which are present in quantities such as ppm (parts per million) or ppb (parts per billion), can be determined. One of the basic premises for the use of a chemical composition analysis on clay deposits and archaeological ceramics samples is that the samples can be better differentiated if the analytical technique has a good sensitivity, precision and accuracy. If an element is not measured with good precision it may hinder the observation of real differences in concentration and the discriminating effect of other well-measured elements tends to be reduced. These small differences can enable the observation of groups with similar composition, since artifacts manufactured with the same or geologically similar raw material source will be more chemically similar than other ones, which were manufactured with a raw material collected in a different geological environment (**MUNITA et al., 2005**). Thus, the determination of the concentration of various elements in the trace level will tend to produce a highly specific "fingerprinter" for a source of clay as raw material.

Other parameter related to the properties of analytical methods is accuracy, which regards the real concentration of an element, a value that does not depend on the applied method. The accuracy of analytical methods is determined by using a reference material, whose element concentrations were previously determined by various analytical methods. In this case NAA has great accuracy for various elements (**GLASCOCK, 1992**). The determination of the analytic precision is also of great importance and must taken into account. Precision in this sense regards the reproducibility of the obtained results and its limitations can derive from inadequate sample preparation, either due to contamination with the same element that is being determined, or due to a non homogeneous sample.

The results obtained by INAA analyses of potsherds for the archaeological sites MS-CP-71 and MS-CP-61 are presented in Table 1. Discriminant analysis was applied in order to obtain more conclusive information from the data set. Therefore, the results were initially transformed to log base10 aiming to compensate for the large differences of magnitudes between the measured elements (**HARBOTTLE, 1976**). The log base 10 transformation of data before a multivariate statistical method is a usual procedure. One reason for that is that within the raw material, elements have a natural log-normal distribution. Another reason is that a logarithmic transformation tends to stabilize the variance of the variables and would thus give them approximately equal weight in an unstandardized multivariate statistical analysis. The multivariate statistical method of data analysis chosen was the discriminant analysis based on its property to maximize the difference between two or more groups, which is based on the fact that principal variance-covariance matrix is an accurate representation of the total variance and covariance.

In Figure 1 the plot of discriminant function 2 *versus* the discriminant function 1 is presented. The data set analyzed encloses all the ceramic samples and only one clay sample, which was included in order to check a possible assemblage. The obtained ellipses represent a confidence level of 95%. Based on this result it is possible to conclude that the pottery coming from the archaeological sites MS-CP-71 and MS-CP-61 can be distinguished based on their elemental composition. At the moment we have analyzed eight clay samples from sources located in the surroundings of the archaeological sites. The comparison of the elemental composition of the sherds and clay sources will be performed in a future work, since it is our intention to analyze the ceramic material of a third archaeological site located in the region of study.

Conclusion

The INAA analysis enabled characterizing the potsherds from the archaeological sites MS-CP-71 and MS-CP-61 concerning some major elements and, most important, also trace element composition. The data treatment by discriminant analysis indicates two distinct groups of samples. The elements responsible for the discrimination of the two groups are Na, Lu, U, Yb, La, Th, Cr, Cs, Sc, Rb, Fe, Eu, Ce, Hf, and Tb. Based on these evidences we suggest that the potters from the pre-colonial population of the two settlements under study made use of different clay sources, most probably collected in the surroundings of each archaeological site.

Acknowledgements
The authors would like to thank to FAPESP (Processo 04/07827-9) and FUNDECT for the financial support.

M. P. Felicissimo
Estudante de Pós-Doutorado no Laboratório de Análise por Ativação Neutrônica. Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP.

J. L. Peixoto
Professor no Departamento de Ciências do Ambiente. Universidade Federal de Mato Grosso do Sul, Campus Universitário de Corumbá.

C.S. Munita
Pesquisador no Laboratório de Análise por Ativação Neutrônica. Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP.

References

BISHOP, R.L.; CANOUTS, V.; CROWN, P.L.; DE ATLEY, S.P. Sensitivity, precision, and accuracy: their roles in ceramic compositional data bases. **American Antiquity,** v. 55, n. 3 p. 537-546, 1990.

DAVIS, M.K.; JACKSON, T.L.; SHACKLEY, M.S.; TEAGUE,T.; HAMPEL, J. Factors affecting the energy-dispersive X-ray fluorescence (EDXRF) analysis of archaeological obsidian. In: **Archaeological Obsidian Studies**. Shackley, M.S. (Ed.). Plenum Press: New York, 1998, p. 159-180.

FELICISSIMO, M.P.; PEIXOTO, J. L. S.; AZIOUNE, A.; PIREAUX, J-J., HOUSSIAU; L.; RODRIGUES-FILHO, U. P. XPS and SIMS applied to the compositional study of Pre-Colonies Potteries from South Pantanal. **Philosophical Magazine A**, v, 84, n. 32, p. 3483-3496, 2004a.

FELICISSIMO, M.P.; RODRIGUES FILHO, U.P.; PEIXOTO, J. L. SEM and EDS mapping as a tool for the study of additives in ancient ceramics from the South-west border of Pantanal. **Acta Microscopica**, Supplement A, p. 285-286, 2001.

FELICISSIMO, M. P.; PEIXOTO, J. L.; RODRIGUES-FILHO, U. P. Archaeometric Studies of Indian Pre-colonial ceramics from lakes Castelo and Vermelha located in the Pantanal of Mato Grosso do Sul. **Canindé – Revista do Museu de arqueologia do Xingó**, v. 4, p. 325-368, 2004b.

GLASCOCK, M.D. Characterization of Archaeological Ceramics at MURR by NAA and Multivariate Statistics. In: **Chemical Characterization of Ceramic Paste in Archaeology**. Monographs in world archaeology. NEFF, H. (Ed.). Prehistory Press: New York, 1992, Section 1, p. 11-26.

HALL, M.; MAEDA, U.; HUDSON, M. Pottery production on Rishiri Island, Japan: perspectives from X-ray fluorescence studies. **Archaeometry,** v. 44, n. 2, p. 213-228, 2002.

HARBOTTLE, G. Activation Analysis in Archaeology. **Radiochemistry: a specialist periodical report**, Newton, G.W.A., (Ed.). The Chemical Society: London, 1976, p. 33-72.

MUNITA, C.S.; PAIVA, R.P.; ALVES, M.A.; OLIVEIRA, P.M.S.; MOMOSE, E.F. Provenance study of archaeological ceramic. **Journal of Trace and Microprobe Techniques,** v. 21, n. 4, p. 697-706, 2003.

MUNITA, C.S.; PAIVA, R.P.; OLIVEIRA, P.M.S.; MOMOSE, E.F.; PLÁ, R.; MORENO, M.; ANDONIE, O.; FALABELLA, F.; MUÑOZ, L.; KOHNENKAMP, I. Intercomparison among three activation analysis laboratories in South America. **Journal of Trace and Microprobe Techniques,** v. 19, n. 2, p. 189-197, 2001.

MUNITA CS, SILVA MA, SILVA FA, OLIVEIRA PMS. Archaeometric study of clay deposits from the indigenous land of the Asurini do Xingu. **Instrumentation Science and Technology,** v. 33, n. 2, p. 161-173, 2005.

PEIXOTO, J.L.S. A ocupação dos povos indígenas pré-coloniais nos grandes lagos do Pantanal Sul-mato-grossense. Tese (Doutorado). Porto Alegre: PUCRS, 2003. 262p.

PILLAY, A.E.; PUNYADEERA, C. An enhanced procedure for the rapid digestion of high silicate archaeological specimen followed by ICP-MS determination of traces of rare earth elements. **Journal of Trace and Microprobe Techniques,** v. 19, p. 225-241, 2001.

SCOTT, D.A. The application of scanning X-ray fluorescence microanalysis in the examination of cultural materials. **Archaeometry,** v. 42, n. 4, p. 475-482, 2001.

Table 1. Results for the elemental composition of pottery from the archaeological sites MS-CP-71 and MS-CP-61 in μg g^{-1}, unless otherwise indicated

A01	0,125	0,430	1,48	3,05	41,34	11,85	53,63	3,86	13,29	84,9	2,48	1,42
A04	0,188	0,476	2,82	3,20	43,86	13,51	79,12	5,91	15,69	128,63	5,81	1,49
A05	0,133	0,523	2,99	3,41	44,57	12,82	56,58	3,69	14,8	88,74	3,85	1,59
A07	0,139	0,446	3,57	2,95	34,19	12,02	57,68	4,25	11,52	103,27	2,76	1,15
A09	0,072	0,473	2,49	2,98	39,25	12,69	45,58	2,99	10,16	111,02	2,84	1,31
A12	0,174	0,495	3,63	3,17	39,25	14,07	63,15	5,55	12,2	198,52	3,97	1,45
A13	0,12	0,237	1,25	1,24	20,51	9,19	60,57	5,27	12,2	100,09	1,87	0,713
A18	0,129	0,607	3,32	4,18	53,72	16,89	79,94	6,07	16,7	142,97	3,11	1,78
A03	0,095	0,392	2,59	2,72	39,32	13,20	77,20	7,20	16,10	173,20	6,70	1,30
A06	0,087	0,393	2,01	2,41	38,44	13,00	75,50	7,80	16,00	164,70	6,70	1,20
A11	0,102	0,331	3,13	2,11	27,73	10,60	43,40	3,30	9,00	107,20	2,50	0,90
A14	0,088	0,396	1,99	2,79	39,43	9,70	33,20	2,20	12,80	39,70	2,80	1,60
A15	0,067	0,421	1,73	2,97	46,56	11,80	45,70	2,80	15,40	62,00	3,30	1,50
A16	0,162	0,584	0,81	3,66	37,34	13,80	65,80	5,00	13,00	124,40	3,30	1,20
A17	0,116	0,620	2,82	3,65	36,72	12,90	49,90	4,10	11,30	111,40	2,50	1,20
A18	0,108	0,560	3,56	3,90	50,48	15,10	72,60	5,70	15,20	120,00	2,80	1,60
A20	0,137	0,609	2,29	4,04	50,39	13,27	77,90	7,90	15,70	197,80	4,40	1,80
A22	0,125	0,336	2,78	2,84	41,65	11,30	35,80	1,90	14,80	106,60	3,50	1,60
A23	0,112	0,438	2,12	2,89	42,15	11,00	37,30	2,60	13,40	99,40	2,90	1,40
A25	0,165	0,450	3,33	3,08	30,87	10,90	43,50	4,40	9,90	94,60	3,50	0,99
A26	0,095	0,630	2,78	4,40	59,69	16,70	64,50	5,00	14,80	167,70	4,10	1,90
A28	0,152	0,629	1,26	4,02	41,95	14,00	48,80	4,30	12,20	211,90	3,30	1,40
A29	0,215	0,607	1,65	4,24	48,77	14,90	62,50	6,40	13,50	243,40	3,50	1,70
A30	0,057	0,532	2,02	3,22	48,81	13,20	43,90	3,30	15,30	65,20	3,40	1,60
A32	0,07	0,60	2,78	4,20	50,40	16,10	67,60	3,00	12,90	34,40	4,20	1,70
A33	0,14	0,40	1,60	2,80	34,20	11,40	58,40	4,70	12,40	110,40	3,40	0,80
A34	0,23	0,40	2,80	3,20	36,50	12,60	66,30	3,50	13,40	164,80	2,70	1,10
A35	0,17	0,60	1,60	4,20	45,00	14,50	49,70	7,00	13,00	298,90	3,40	1,50
A36	0,11	0,70	2,50	4,70	62,30	16,80	61,90	10,40	14,90	111,40	5,50	1,90
A37	0,16	0,40	2,20	2,90	36,30	11,50	63,30	3,70	10,90	120,90	2,10	1,20
A38	0,11	0,50	2,80	2,50	31,50	10,90	53,90	5,70	11,40	116,40	3,30	0,93
A39	0,11	0,60	4,20	3,70	47,20	15,70	83,40	8,00	17,60	42,50	5,40	1,30
A40	0,08	0,60	4,40	3,90	55,80	16,80	91,00	10,80	20,20	50,80	4,50	1,60
A41	0,13	0,40	2,50	2,70	36,70	10,00	54,70	4,80	11,70	93,70	2,40	1,10
A44	0,11	0,50	6,10	3,90	41,30	14,80	68,40	6,10	13,30	57,10	5,30	1,20
A45	0,01	0,50	3,70	3,10	34,20	13,00	73,20	7,00	14,80	44,80	5,00	1,20
A53	0,11	0,50	4,30	3,60	47,40	15,10	87,90	5,70	16,80	54,70	6,40	1,50
B01	0,07	0,70	4,40	4,40	62,10	16,50	69,90	6,90	15,50	72,00	2,60	2,10
B02	0,07	0,60	4,20	4,10	43,60	17,00	78,10	6,20	15,30	112,50	5,20	1,50

Table 1. Continued

Sample	Na(%)	Lu	U	Yb	La	Th	Cr	Cs	Sc	Rb	Fe(%)	Eu
B03	0,07	0,70	6,10	4,40	55,60	17,10	75,80	6,90	15,00	87,70	4,40	1,70
B05	0,09	0,70	4,40	4,30	49,50	15,60	74,00	6,10	14,50	92,50	3,80	1,60
B06	0,07	0,60	4,00	3,60	42,00	13,60	63,20	4,90	14,40	90,10	3,20	1,40
B09	0,09	0,60	4,60	3,60	36,50	14,10	60,40	5,80	11,70	143,00	3,10	1,30
B10	0,09	0,70	6,80	4,30	53,30	17,50	74,30	5,60	15,80	105,20	5,40	1,70
B11	0,1	0,60	3,10	3,70	39,20	12,80	53,10	6,80	11,60	126,90	3,80	1,20
B07	0,067	0,798	2,83	5,11	68,37	15,69	79,53	6,57	15,42	105,75	6,47	2,53
B12	0,088	0,854	3,03	5,40	70,71	16,91	83,38	7,23	16,16	129,61	6,64	2,7
B13	0,088	0,546	2,46	3,77	43,80	15,37	78,91	7,87	15,69	123,16	3,74	1,54
B14	0,062	0,692	3,87	4,24	44,23	16,75	81,39	8,19	16,19	147,11	4,41	1,74
B15	0,094	0,813	4,10	4,74	56,26	16,17	76,01	7,32	15,17	126,54	4,62	1,99
B17	0,115	0,579	2,81	3,82	41,99	14,08	72,19	5,23	13,76	94,23	3,31	1,4
B18	0,087	0,675	5,73	4,26	52,17	15,65	75,42	5,64	14,75	89,17	4,13	1,83
R01	0,078	0,605	2,76	3,61	39,72	11,7	49,51	4,28	10,56	65,01	3,8	1,36
R02	0,046	0,805	3,48	4,46	66,18	18,03	74,21	9,37	16,24	60,09	2,03	2,24
R03	0,041	0,664	3,77	3,79	44,94	15,19	65,5	5,97	14,55	20,52	4,93	1,45
R05	0,018	0,504	2,74	2,68	29,43	14,59	64,32	5,57	12,88	33,24	3,00	0,93
R06	0,070	0,673	2,60	3,72	38,02	12,92	55,08	4,53	10,89	43,54	3,28	1,30
R07	0,124	0,741	5,32	4,46	57,55	18,16	73,56	8,40	15,94	79,31	3,72	1,53
R08	0,042	0,843	4,45	4,13	59,98	21,73	88,72	8,86	18,66	144,36	3,76	1,67
R04	0,039	0,627	6,03	3,83	44,88	15,60	68,00	5,70	13,20	47,10	2,80	1,40

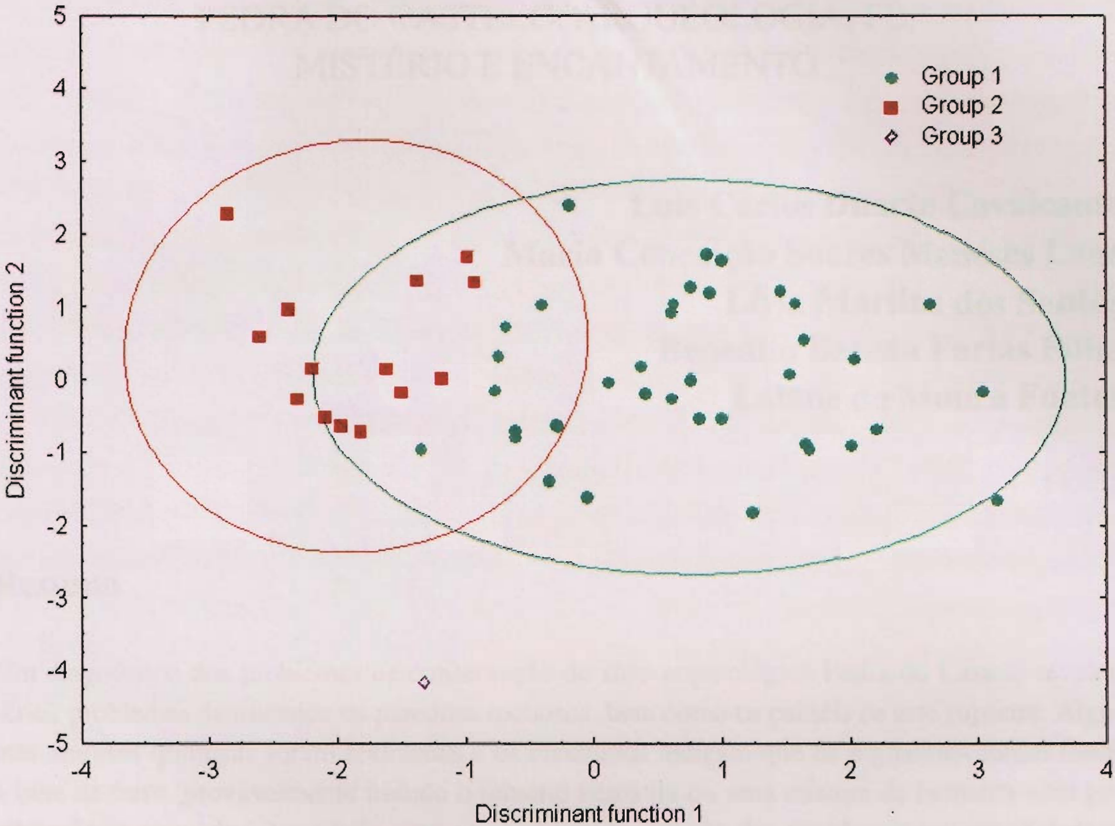

Figure 1: Discriminat functions for pottery samples from the archaeological sites MS-CP-71, group1, and MS-CP-61, group 2, group 3 is represented by a single clay sample. Ellipses represent a confidence level of 95%.